OIPE JC26
MAY 31 2005
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DECLARRATION

I, Atsushi ONOGI, the translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is a true English translation of Japanese Patent Application No. 2002-347478.

Signed, this twentieth day of May, 2005

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[Name of Document] Application for Patent
[Reference No.] 0110064
[Date of Filing] November 29, 2002
[Addressee] Commissioner of Japan Patent Office
[Int' l Class] G03G 9/08
[Title of the Invention] Dry toner
[Number of Claims] 14
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[Prepayment No.]	009036
[Amount of Payment]	21,000 Yen
[List of Attached Documents]	
[Name of Document]	Specification 1
[Name of Document]	Drawings 1
[Name of Document]	Abstract 1
[General power of Attorney No.]	9909722
[Necessity of Proof]	Necessary
[Name of Document]	Specification
[Title of the Invention]	Dry toner

[Scope of Claims]

[Claim 1] A dry toner prepared by a method comprising:

dissolving or dispersing a toner composition in an organic solvent to prepare a toner composition liquid; and

dispersing the toner composition liquid in an aqueous liquid, the aqueous liquid comprising:

a binder resin comprising a modified polyester (i); and

a carbon black which has a pH not greater than 7,

the toner being characterized by having a volume average particle diameter (Dv) of from 3 to 7 µm and a ratio (Dv/Dp) of the volume average particle diameter (Dv) to a number average particle diameter (Dp) of from 1.00 to 1.25.

[Claim 2] The dry toner according to Claim 1, which is characterized in that the toner composition comprises a prepolymer and the modified polyester (i) is formed by the prepolymer in the steps of dissolving or dispersing the toner composition in the organic solvent and dispersing the resultant in the aqueous medium.

[Claim 3] The dry toner according to Claim 1 or 2, which is characterized in that the carbon black is used as a master batch in which the carbon black is dispersed in a resin.

[Claim 4] The dry toner according to Claim 3, which is characterized in that the resin used in the master batch is a polyester resin.

[Claim 5] The dry toner according to any one of Claims 1 to 4, which is characterized in that the toner binder resin further comprises an unmodified polyester (ii) and a weight ratio (i/ii) of the modified polyester (i) to the unmodified polyester (ii) is from 5/95 to 80/20.

[Claim 6] The dry toner according to Claim 5, which is characterized in that the unmodified polyester (ii) has an acid value of from 1 to 15 mgKOH/g.

[Claim 7] The dry toner according to Claim 5 or 6, which is characterized in that the unmodified polyester (ii) has a peak molecular weight of from 1000 to 30000.

[Claim 8] The dry toner according to any one of Claims 5 to 7, which is characterized in that the unmodified polyester (ii) has a glass transition temperature (Tg) of from 35 to 55 °C.

[Claim 9] The dry toner according to any one of Claims 1 to 8, which is characterized in that the toner has a spindle shape.

[Claim 10] The dry toner according to Claim 9, which is characterized in that the spindle shape of the toner has a ratio (r2/r1) of a minor axis particle diameter (r2) to a major axis particle diameter (r1) of from 0.5 to 0.8 and has a ratio (r3/r1) of a thickness (r3) to the minor axis particle diameter (r2) of from 0.7 to 1.0.

[Claim 11] A developer which is characterized by comprising the dry toner set forth in any one of Claims 1 to 10.

[Claim 12] A toner container which is characterized by containing the dry toner according to any one of Claims 1 to 10.

[Claim 13] An image forming method, which is characterized by comprising the step of using the developer set froth in Claim 11.

[Claim 14] An image forming apparatus, which is characterized in that the toner set forth in Claim 11 is installed therein.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a dry toner for developing an electrostatic image in electrophotography, electrostatic recording, electrostatic printing and the like, a developer including the dry toner, an image forming method using the developer and an image forming apparatus using the developer. More particularly the present invention relates to a dry toner, a developer, an image forming method and an image forming apparatus for use in copiers, laser printers and plain-paper facsimile machines and similar devices which use a direct or indirect electrophotographic development method.

[0002]

[Background Art]

A developer for use in electrophotography, electrostatic recording, electrostatic printing and the like is adhered in the developing process, for example, to an image bearing member such as a photoreceptor on which an electrostatic image is formed, is next transferred in the transfer process from the photoreceptor to a transfer medium such as transfer paper and then is fixed on the paper in the fixing process. As a developer for developing an electrostatic images formed on the surface carrying a latent image thereon, there are a two component developer containing a carrier and a toner, and a single component toner requiring no carrier (a magnetic toner and a non-magnetic toner).

Conventional dry toners for use in electrophotography, electrostatic recording and electrostatic printing are typically prepared by fusing/kneading toner binders such as styrene-containing resins and polyesters with a colorant and so on followed by finely pulverizing.

[0003]

(Problems with reference to fixability)

These dry toners are fixed by heating and fusing with a heat roll after the toners are developed and transferred onto a medium such as paper. When the temperature of the heat roll is too high while fixing, a hot offset problem tends to occur in which the toner is excessively fused and adhered to the heat roll. When the temperature of the heat roll is too low, there is a problem in that the toner does not fuse sufficiently, resulting in inadequate fixing. In the light of energy saving and miniaturization of devices such as copiers, a toner is desired which has a high hot offset temperature (hot offset resistance) and has a low fixing temperature (fixability at a low temperature). In addition, the toner is required to have a preservability against hot temperature in order that the blocking does not occur at an atmospheric temperature while the toner is stored or while the toner is installed in the device.

[0004]

(Problems with reference to particle diameter and shape)

Toner particle diameters become smaller and smaller in order to improve images by giving high quality and high resolution. However, a toner which is manufactured by a conventional kneading and pulverization method has an irregular shape. Such a toner is fractured in a machine when the toner is stirred with a carrier or contacts with a developing roller, a toner furnishing roller, a layer regulating blade and a triboelectrical charging blade so that extremely fine particles are generated and fluidizer is buried in the toner surface, resulting in deterioration of image qualities. In addition, due to its shape, fluidity of the toner as powder is so bad that a large amount of fluidizer has to be included therein, and the toner has a large volume when the toner is filled in a toner bottle, which is a barrier for miniaturization.

[0005]

Furthermore, since the process for transferring toner images from a photoreceptor to a transfer medium or paper becomes complicated, problems occur such as image omission due to poor transferability stemming from irregular shapes of pulverized toners and an increase of toner consumption to compensate the image omission.

[0006]

Therefore, there is an increasing demand for high definition images without omission and lower running cost by further improving transfer efficiency and reducing the amount of toner consumption. This is because if transfer efficiency is extremely excellent, an image forming apparatus does not need to have a cleaning unit for removing untransferred toner from a photoreceptor or a transferring medium so that the device can be miniaturized and cost can be reduced. Further, there is another merit that no waste toner is generated. In order to avoid the problems arisen from irregularity in shape of the toner, various kinds of methods of manufacturing spherical toners have been proposed.

[0007]

In order to solve the problems mentioned above, the following toners have been proposed particularly for obtaining a good combination of high temperature resistance, low temperature fixability and hot offset resistance. For example, (1) a toner including a polyester used as a toner binder which is partially cross-linked by multifunctional monomers is proposed in published unexamined Japanese Patent Application No. (hereinafter referred to as JOP.) 57-109825 and (2) a toner including a urethane modified polyester as a toner binder is proposed in JOP. 7-101318. In addition, (3) a full color toner prepared by granulating fine polyester particles and fine wax particles is proposed in JOP. 7-56390 in order to reduce the amount of an oil which is applied to a heat roll.

[0008]

Further, in order to improve powder fluidity and transferability of a toner having a small particle, (4) a toner polymerized by suspension polymerization after dispersing a vinyl monomer composition including a colorant, a polar resin and a release agent in water is proposed in JOP. 9-43909 and in addition, (5) a toner including a polyester resin which is dispered in water to granulate a spherical toner using a solvent is proposed in JOP. 9-34167.

Furthermore, (6) a substantially spherical dry toner made of a polyester resin which is modified by urea linkage is disclosed in JOP. 11-133666.

[0009]

However, the toners disclosed in (1) to (3) have such insufficient fluidity and transferability that it is very difficult to obtain quality images even when the toners have a small particle. Further, the toners disclosed in (1) and (2) are not suitable for practical use because of their not having a good combination of high temperature preservability and low temperature fixability and because of their producing images having unsatisfactory gloss when used as a full color toner. In addition, the toner disclosed in (3) is insufficient in low temperature fixability and further is not satisfactory in the light of hot offset resistance for oil-free fixing. The toners disclosed in (4) and (5) have improved powder fluidity and transferability. However, the toner disclosed in (4) has a problem in that large energy is required for fixing because the lowtemperature fixability thereof is insufficient. This becomes a large problem especially when the toner is used as a full-color toner. The toner disclosed in (5) is superior in low temperature fixability but insufficient in hot offset resistance so that it is impossible to eliminate oil application to a heat roll when the toner is used as a full-color toner.

Furthermore, the toner disclosed in (6) is excellent in producing images having adequate gloss and good releasability when used as a full-color toner because viscoelasticity of the toner can be controlled by a polyester elongated by urea linkage. Especially the toner disclosed in (6) is effective in alleviating "electrostatic offset" by which toners on an unfixed image on a transfer medium electrostatically scatters or adheres to a fixing roller when the fixing roller is electrostatically charged. This "electrostatic offset" is prevented by electrical neutralization between positive chargeability created by the urea linkage portions of the polyester resin included in the toner (6) and weak negative chargeability of the polyester resin per se. Although the toner has the advantages mentioned above, the toner is fractured in an image forming apparatus when the toner is stirred with a carrier or contacts with a developing roller, a toner furnishing roller, a toner layer regulating blade and a triboelectrically charging blade. Thereby, extremely fine particles tend to be generated and a fluidizer on the surface of the toner is buried in the toner. This results in problems such as deterioration of image qualities and a shortening of toner life.

[0010]

[Patent Document 1]

Published unexamined Japanese Patent Application No. 11-133666.

[0011]

[Problems to be Solved]

One object of the present invention is to provide a dry toner having a small particle diameter, a high electric resistance, a long life and excellent powder fluidity, transferability, high temperature resistance, low temperature fixability and hot offset resistance, a developer including the dry toner, a toner container which contains the dry toner and an image forming method and apparatus using the developer.

[0012]

[Means for Solving the Problems]

Namely, according to the present invention, the following is provided:

(1) a dry toner prepared by a method including the steps of dissolving or dispersing a toner composition in an organic solvent to prepare a toner composition liquid and dispersing the toner composition liquid in an aqueous liquid. The aqueous liquid contains a binder resin including a modified polyester (i) and a carbon black which has a pH not greater than 7. The toner is characterized by having a volume average particle diameter (Dv) of from 3 to 7 µm and a ratio (Dv/Dp) of the volume average particle diameter (Dv) to a number average particle diameter (Dp) of from 1.00 to 1.25;

(2) the dry toner set forth in (1), which is characterized in that the toner composition includes a prepolymer and the modified polyester (i) is formed by the prepolymer in the steps of dissolving or dispersing the toner composition in the organic solvent and dispersing the resultant in the aqueous medium;

(3) the dry toner set forth in (1) or (2), which is characterized in that the carbon black is used as a master batch in which the carbon black is dispersed in a resin;

(4) the dry toner set forth in (3), which is characterized in that the resin used in the master batch is a polyester resin;

(5) the dry toner set foth in any one of (1) to (4), which is characterized in that the toner binder resin further contains an unmodified polyester (ii) and a weight ratio (i/ii) of the modified polyester (i) to the unmodified polyester (ii) is from 5/95 to 80/20;

(6) the dry toner set forth in (5), which is characterized in that the unmodified polyester (ii) has an acid value of from 1 to 15 mgKOH/g;

(7) the dry toner set forth in (5) or (6), which is characterized in that the unmodified polyester (ii) has a peak molecular weight of from 1000 to 30000;

(8) the dry toner set forth in any one of (5) to (7), which is

characterized in that the unmodified polyester (ii) has a glass transition temperature (Tg) of from 35 to 55 °C;

(9) the dry toner set forth in any one of (1) to (8), which is characterized in that the toner has a spindle shape;

(10) the dry toner set forth in (9), which is characterized in that the spindle shape of the toner has a ratio (r2/r1) of a minor axis particle diameter (r2) to a major axis particle diameter (r1) of from 0.5 to 0.8 and has a ratio (r3/r1) of a thickness (r3) to the minor axis particle diameter (r2) of from 0.7 to 1.0;

(11) a developer which is characterized by containing the dry toner set forth in any one of (1) to (10);

(12) a toner container which is characterized by containing the dry toner set forth in any one of (1) to (10);

(13) an image forming method, which is characterized by including the step of using the developer set froth in (11); and

(14) an image forming apparatus, which is characterized in that the toner set forth in (11) is installed therein.

[0013]

[Description of the Preferred Embodiment]

The present invention will be described in detail below.

The dry toner of the present invention is prepared by dissolving or dispersing a toner composition in an organic solvent and dispersing the resulting toner composition liquid in an aqueous medium. The dry toner contains at least a modified polyester (i) and a carbon black which has a PH of not greter than 7 and preferably from 2 to 6. The toner has a volume average particle diametr of from 3 to 7 μm and the ratio (Dv/Dp) of Dv to a number average particle diameter (Dp) is from 1.00 to 1.25, and preferably from 1.05 to 1.25. The dry toner has a high electric resistance and is excellent in powder fluidity, transferability, high temperature preservability, low temperature fixability and hot offset resistance.

When a two component developer including the toner is used and repeatedly replenished for an extended period of time, the variance in the particle diameter of the toner in the developer is small. In addition, the developability of the toner is good and stable when the toner is repeatedly agitated in the developing unit over a long period of time. When the toner is used as a single component developer and repeatedly replenished for an extended period of time, the variance in the particle diameter of the toner is small and filming of the toner on a developing roller and fusion bonding of the toner onto a member such as a blade for regulating the thickness of the toner layer do not occur. Therefore, good and stable developability and images are obtained when the toner is repeatedly agitated in a developing unit for an extended period of timer.

[0014]

It is generally said that a toner having a small particle diameter is advantageous to obtain high definition and high quality images, but is disadvantageous in transferability and cleaning properties. When a two component developer including a toner which has a volume average particle diameter smaller than the lower limit for the toner of the present invention is used, the toner used is fusion bonded to the surface of the carrier while the developer is repeatedly stirred for a long period of time and therefore charging ability of the carrier weakens. In contrast, when a toner having a volume average particle diameter smaller than the lower limit for the toner of the present invention is used as a single component developer, filming of the toner on a developing roller and fusion bonding of the toner onto a member such as a blade for regulating the thickness of the toner layer tend to occur.

These phenomena apply not only to the toner having a particle diameter smaller than the lower limit for the toner of the present invention but also to a toner in which fine particles occupy a high content rate.

[0015]

To the contrary, when a toner has a particle diameter larger than the allowable range for the toner of the present invention, images having a high definition and high quality tend to be hard to obtain. In addition, the particle diametr of such a toner tends to vary on a large scale when the toner contained in a developer is replenished. It is also found that this applies to the case of a toner having a ratio of the volume average particle diameter thereof to the number average particle diameter thereof greater than 1.25.

It is preferable that a toner have a ratio of the volume average particle diameter thereof to the number average particle diameter thereof less than 1.05 and especially less than 1.00 in the light of stability of toner behavior and uniformity in the amount of charge of the toner. However, it is found that the yield of the toner having the ratio of less than 1.05, especially less than 1.00, is extremely poor, which gives rise to a cost problem.

[0016]

It is also found that the toner prepared by the manufacturing method according to the present invention, in which a toner material component is dissolved or dispersed in an organic solvent and further dispersed in an aqueous liquid, has a small particle diameter with a sharp particle diameter distribution. However, there is a problem in that a colorant in the toner, especially carbon black, is insufficiently dispersed compared with a toner prepared by kneading and pulverization. After an intensive study by the present inventors for solving this problem, it is found that a carbon black having a pH not greater than 7, and preferably of from 2 to 6, disperses in the toner well even when the carbon black is dispersed in an organic solvent. By following this way, a toner having a high electric resistance with excellent fluidity and transferability can be obtained.

[0017]

Dispersibility of a carbon black in a toner can be improved by using a master batch in which the carbon black is dispersed in a resin in advance.

Further, it is found that, when a polyester resin is used as the resin in the master batch, dispersibility of the carbon black in the toner is improved.

[0018]

A preferred example of the dry toner of the present invention will be described next.

It is preferable that the dry toner according to the present invention have a spindle shape.

A toner having an irregular or flat shape has a poor powder fluidity. Therefore such a toner easily causes problems such as background fouling which is caused by the fact that triboelectric charging is not smoothly performed, poor reproduction for a latent image having a fine dot which is caused by the fact that the toner is hard to have a dense and uniform configuration, and inferior transfer efficiency in transferring toner images by an electrostatic transfer method which is caused by the fact that lines of electric force hardly affect the toner.

In contrast, a toner having a substantially spherical shape has too good powder fluidity and thereby excessively reacts against external forces. This causes a problem in that the toner particles easily scatter outside a dot at the time of developing and transferring. Spherical toners have another problem in that since the toners easily roll on a photoreceptor and sneak between the photoreceptor and a cleaning member, cleaning performance often becomes poor.

[0019]

Fluidity of the spindle shaped toner of the present invention is so properly adjusted that triboelectric charging is smoothly performed, resulting in formation of images with no background fouling. Therefore minute dots can be orderly developed with the toner and the toner image is efficiently transferred, resulting in superior dot reproduction. In addition, the proper fluidity prevents toner scattering at this time. Also a spindle shaped toner generally has a limited number of axes, around which the toner particle revolves, compared with a spherical toner particle. Therefore, a poor cleaning performance caused by toner particles sneaking under a cleaning member rarely occurs.

[0020]

The toner shape will be described with reference to Figs. 1(a) and 1(b).

The toner of the present invention preferably has a spindle shape having a ratio (r2/r1) of from 0.5 to 0.8, more preferably from 0.5 to 0.7, wherein r2 is the minor axis particle diameter and r1 is the major axis particle diameter, and a ratio (r3/r2) of from 0.7 to 1.0, more preferably from 0.8 to 1.0, wherein r3 is the thickness thereof and r2 is the minor axis particle diameter. When the ratio (r2/r1) is not greater than 0.5, cleaning performance is good since the toner shape is away from being spherical. However, the toner tends to have poor dot representation and transfer efficiency, resulting in formation of low quality images. In contrast, when the ratio (r2/r1) is greater than 0.8, the toner shape is nearer to a spherical shape, and therefore the toner tends to provide especially bad cleaning performance in a low temperature/humidity environment.

In addition, when the ratio (r3/r2) is not greater than 0.7, the toner shape is near to a flat form so that toner scattering hardly occurs as in the case of a toner having an irregular shape but a high transfer rate cannot be obtained unlike the case of a toner having a spherical shape. Especially when the ratio (r3/r2) of thickness to minor axis particle diameter is 1.0, the toner particle revolves around the major axis thereof. When a toner has a spindle shape with the ratio (r3/r2) of 1.0, the toner shape is not irregular, flat or spherical. Therefore, the toner can have all the advantages of both shapes, i.e., a good combination of triboelectric charging, dot reproduction, transfer efficiency, toner scattering avoidability and cleanability.

The particle dimensions, r1, r2 and r3 of the toner can be determined by taking photos of the toner particles using a scanning electron microscope (SEM) while observing the particles from different angles.

[0021]

(Modified polyesters)

The modified polyesters for use as a binder resin of the dry toner of the present invention are polyesters which have functional groups other than the functional groups contained in acid and alcohol monomer units or bonding groups other than the ester bonding group, or polyesters with which a resin component different from those of the polyesters is bonded by covalent bonding or ionic bonding.

Specific examples thereof include polyester resins having an end which is formed by a bonding other than ester linkage. Such polyester resins can be prepared, for example, by incorporating a functional group such as isocyanate groups, which can react with acid groups and hydroxyl groups, at the end of a polyester and reacting the functional group with an active hydrogen compound to perform a modification or elongation reaction.

Further, by using a compound having a plurality of active hydrogen atoms, ends of polyesters can be bonded with each other. The thus prepared urea modified polyesters, urethane modified polyesters and so on, can also be readily used as the modified polyesters.

Modified polyesters can also be prepared by introducing a reactive group such as double bond within the main chain of a polyester resin and performing a radical polymerization reaction thereon to graft a component having C-C bonding or bridging double bonds at a branch chain. Styrene modified polyesters and acrylic modified polyesters are examples of these types of modified polyesters that can also be used as the modified polyester.

Also polyester resins which have a different resin unit within the main chain thereof through copolymerization or polyester resins which are prepared by reacting an end of a polyester with a carboxyl group or a hydroxyl group can be used as the modified polyester.

Specific examples thereof include a modified polyester which is copolymerized with a silicone resin having ends which are modified by a carboxyl group, a hydroxyl group, an epoxy group or a mercapto group (e.g., silicone modified polyesters).

Specific preferred examples will be described as follows.

[0022]

(A synthetic example of polystyrene modified polyesters)

A polystyrene graft modified polyester (i) can be obtained, for example, as follows.

(1) The following components are placed in a reacting container having a condenser, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230 °C under normal pressure.

Adduct of bisphenol A with 2 moles of ethylene oxide	724
Isophthalic acid	200
Fumaric acid	70
Dibutyl tin oxide	2

(2) The reaction is further performed for 5 hours under a reduced pressure of from 10 to 15 mmHg.

(3) Subsequent to cooling down to 160 °C, 32 parts of phthalic anhydride are added thereto and the resulting mixture allowed to react for 2 hours.

(4) Subsequent to cooling down to 80 °C, 200 parts of styrene, 1 part of benzoyl peroxide and 0.5 parts of dimethyl aniline are mixed with the reaction product in ethyl acetate and the resulting mixture allowed to react for 2 hours.

(5) Ethyl acetate is removed from the reaction product by distillation.

Thus a polystyrene graft modified polyester (i) having an average molecular weight of 92000 is prepared.

[0023]

(Urea modified polyester)

Specific examples of a urea modified polyester (i) include a reactant of a polyester prepolymer (A) having an isocyanate group with amine (B). Specific examples of the polyester prepolymer (A) having an isocyanate group include polyesters prepared by reacting an active hydrogen group of a polycondensation compound of a polyol (1) and a polycarboxylic acid (2) with a polyisocyanate (3). Specific examples of the active hydrogen group contained in the polyesters mentioned above include hydroxyl groups (alcohol hydroxyl groups and phenol hydroxyl groups), amino groups, carboxylic groups and mercarpto groups. Among these, alcohol hydroxyl groups are preferable.

[0024]

Specific examples of the polyol (1) are diols (1-1) and polyols (1-2) having at least 3 hydroxyl groups. A diol (1-1) alone or in combination with a small quantity of one or more polyols (1-2) are preferable as the polyol (1). Specific preferred examples of the diols (1-1) are alkylene glycols (e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol and 1,6-hexan diol), alkylene ether glycol (e.g., diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, and polytetra methylene ether glycol), alicyclic diols (e.g., 1,4-cyclo hexane dimethanol, hydrogen added bisphenol A, and bisphenol groups (bisphenol A, bisphenol F and bisphenol S), adducts of the alicyclic diols mentioned above with alkylene oxides (e.g., ethylene oxides, propylene oxides, butylene oxides), and the bisphenols mentioned above with alkylene oxides (e.g., ethylene oxides, propylene oxides and butylene oxides). Among these, alkylene glycols having 2 to 12 carbon atoms and adducts of bisphenol groups with alkylene oxides are preferable, and adducts of bisphenol groups with alkylene oxides and combinations of adducts of one or more bisphenols with one or more alkylene oxides and alkylene glycols having 2 to 12 carbon atoms are especially preferable. Specific examples of the polyols (1-2) having at least 3 hydroxyl groups include aliphatic alcohols having 3 or more hydroxyl groups (e.g., glycerine, trimethylol ethane, trimethylol propane, pentaerythritol and sorbitol), polyphenols having at least

3 hydroxyl groups (e.g., trisphenol PA, phenol novolak and cresol novolak) and adducts of polyphenols having at least 3 hydroxyl groups with the alkylene oxides mentioned above.

[0025]

Specific examples of the polycarboxylic acid (2) are dicarboxylic acids (2-1) and polycarboxylic acids (2-2) having at least 3 hydroxyl groups, with a dicarboxylic acid (2-1) alone or in combination with a small quantity of one or more polycarboxylic acids (2-2) being preferable as the polycarboxylic acid (2). Specific preferred examples of dicarboxylic acid (2-1) include alkylene dicarboxylic acid (e.g., succinic acid, adipic acid and sebacic acid), alkenylene dicarboxylic acid (e.g., maleic acid and fumaric acid), and aromatic dicarboxylic acids (e.g., phthalic acid, isophthalic acid, terephthalic acid and naphthalene dicarboxylic acid). Among the diacids, the alkenylene dicarboxylic acids having 4 to 20 carbon atoms and the aromatic dicarboxylic acids having 8 to 20 carbon atoms are preferable. Specific preferred examples of polycarboxylic acids (2-2) having at least 3 carboxyl groups include aromatic polycarboxylic acid having 9 to 12 carbon atoms (e.g., trimellitic acid and pyromellitic acid). In addition, the polycarboxylic acids (2) can be obtained by reacting acid anhydrides or lower alkyl esters (e.g., methyl esters, ethyl esters and isopropyl esters) of the above-mentioned with the polyols (1).

[0026]

The mixing ratio of the polyol (1) to the polydicarboxylic acid (2), i.e., the equivalent ratio ([OH]/[COOH]) of a hydroxyl group [OH] to a carboxyl group [COOH], is normally from 2/1 to 1/1, preferably from 1.5/1 to 1/1, and more preferably from 1.3/1 to 1.02/1.

[0027]

Specific preferred examples of the polyisocyanate (3) include aliphatic polyisocyanates (e.g., tetramethylene diisocyanate, hexamethylene diisocyanate and 2,6-diisocyanate methylcaproate); alicyclic polyisocyanates (e.g., isophorone diisocyanate and cyclohexyl methane diisocyanate); aromatic diisocyanates (e.g., tolylene diisocyanate and diphenylmethane diisocyanate); aromatic aliphatic diisocyanates (e.g., α, α, α', α'-tetramethyl xylylene diisocyanate); isocyanurates; and blocked polyisocyanates in which the polyisocyanates mentioned above are blocked with phenol derivatives, oximes or caprolactams. These compounds can be used alone or in combination.

[0028]

The mixing ratio of the polyisocyanate (3) to the polyester, i.e., the equivalent ratio ([NCO]/[OH]) of an isocyanate group [NCO] to a hydroxyl group [OH] of a polyester having hydroxyl groups, is normally from 5/1 to 1/1, preferably from 4/1 to 1.2/1, and more preferably from 2.5/1 to 1.5/1. When the [NCO]/[OH] ratio is greater than 5, the low temperature fixability of the toner tends to deteriorate. When the equivalent ratio of [NCO]/[OH] is less than 1, the urea content in the resultant modified polyesters decreases and thereby the hot-offset resistance of the toner tends to deteriorate.

[0029]

The content of the constitutional component, which is obtained from the polyisocyanate (3), in the prepolymer (A) having an isocyanate group at its end portion is from 0.5 to 40 % by weight, preferably from 1 to 30 % by weight and more preferably from 2 to 20 % by weight. When the content is less than 0.5 % by weight, the hot offset resistance of the toner tends to deteriorate and in addition it is hard for the toner to have good heat resistance and low temperature fixability. In contrast, when the content is greater than 40 % by weight, the low temperature fixability of the toner tends to deteriorate.

[0030]

The number of isocyanate groups included in the prepolymer (A) per molecule is normally not less than 1, preferably from 1.5 to 3, and more preferably from 1.8 to 2.5. When the number of isocyanate groups is less than 1 per molecule, the molecular weight of the modified polyester tends to decrease and thereby the hot offset resistance tends to deteriorate.

[0031]

Specific preferred examples of the amine (B) include diamines (B1), polyamines (B2) having three or more amino groups, amino alcohols (B3), amino mercaptans (B4), amino acids (B5) and blocked amines (B6) in which the amines (B1-B5) mentioned above are blocked. Specific preferred examples of the diamines (B1) include aromatic diamines (e.g., phenylene diamine, diethyltoluene diamine and 4,4′-diaminodiphenyl methane); alicyclic diamines (e.g., 4,4′-diamino-3,3′-dimethyldicyclohexyl methane, diaminocyclohexane and isophoron diamine); aliphatic diamines (e.g., ethylene diamine, tetramethylene diamine and hexamethylene diamine); etc. Specific examples of the polyamines (B2) having three or more amino groups include diethylene triamine, triethylene tetramine.

Specific preferred examples of the amino alcohols (B3) include ethanol amine and hydroxyethyl aniline. Specific examples of the amino mercaptan (B4) include aminoethyl mercaptan and aminopropyl mercaptan. Specific preferred examples of the amino acids (B5) include amino propionic acid and amino caproic acid. Specific examples of the blocked amines (B6) of B1 to B5 include ketimine compounds which are prepared by reacting one of the amines B1-B5 mentioned above with a ketone such as acetone, methyl ethyl ketone and methyl isobutyl ketone; oxazoline compounds, etc. Among these amines(B), B1 and a mixture of B1 and a small quantity of B2 are preferred.

[0032]

The molecular weight of the modified polyesters can be controlled using a molecular-weight control agent, if desired.

Specific preferred examples of the molecular-weight control agent include monoamines (e.g., diethyle amine, dibutyl amine, butyl amine and lauryl amine), and blocked amines (i.e., ketimine compounds) prepared by blocking the monoamines mentioned above.

[0033]

The mixing ratio of the amines (B) to the prepolymer (A), i.e., the equivalent ratio ([NCO] /[NHx]) of the isocyanate group [NCO] contained in the prepolymer (A) to the amino group [NHx] contained in the amines (B), is normally from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5 and more preferably from 1.2/1 to 1/1.2. When the mixing ratio is greater than 2 or less than 1/2, the molecular weight of the resultant urea-modified polyester (i) decreases, resulting in deterioration of the hot offset resistance of the resultant toner.

[0034]

In the present invention, the modified polyester (i) can include a urethane linkage as well as a urea linkage. The molar ratio (urea/urethane) of the urea linkage to the urethane linkage is from 100/0 to 10/90, preferably from 80/20 to 20/80 and more preferably from 60/40 to 30/70. When the content of the urea bonding is less than 10%, the hot offset resistance of the resultant toner deteriorates.

[0035]

The modified polyester (i) can be prepared, for example, by a method such as one-shot methods or prepolymer methods. The weight average molecular weight of the modified polyester (i) is not less than 10,000, preferably from 20,000 to 10,000,000 and more preferably from 30,000 to 1,000,000. When the weight average molecular weight is less than 10,000, the hot offset resistance of the resultant toner deteriorates. When an unmodified polyester (ii) described later is used in combination with the modified polyester (i), the number average molecular weight of the modified polyester (i) is not particularly limited if the weight average molecular weight mentioned above is allowed. When the modified polyester (i) is used alone, the number average molecular weight is normally not less than 20000, preferably from 1000 to 10000 and more preferably from 2000 to 8000. When the number average molecular weight is greater than 20000, low temperature fixability of the resultant toner deteriorates and, in addition, the gloss properties thereof also deteriorate when the toner is used in a full color device.

[0036]

(Unmodified polyester)

In the present invention, not only can the modified polyester (i) mentioned above be used alone as a toner binder constituent, but also the unmodified polyester (ii) can be contained as a binder resin in combination with the modified polyester (i). The combined use of (i) and (ii) can improve low temperature fixability and therefore is preferable to the single use of (i) alone. Specific preferred examples of the unmodified polyester (ii) include polycondensation products of polyol (1) and polycarboxylic acid (2) as mentioned above for use in the polyester constituents of the modified polyester (i) mentioned above. It is preferable that (i) and (ii) be at least partially mixed with each other in light of the desired low temperature fixability and hot offset resistance properties. Therefore, it is preferable, but not mandatory, that the unmodified polyester (ii) have a similar composition to that of the polyesters of (i).

[0037]

The weight ratio of (i)/(ii) is normally from 5/95 to 80/20, preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75 and even more preferably from 7/93 to 20/80. When the content of the modified polyester (i) is less than 5% by weight, the hot offset resistance of the toner tends to deteriorate and in addition it is hard for the toner to have both the high temperature preservability and low temperature fixability desired.

[0038]

The peak weight average molecular weight of the unmodified polyester (ii) is normally from 1000 to 30000, preferably from 1500 to 10000 and more preferably from 2000 to 8000. When the peak molecular weight is less than 1000, the high temperature preservability deteriorates. When the peak molecular weight is greater than 10000, the low temperature fixability deteriorates. The hydroxyl group value of the unmodified polyester (ii) is preferably not less than 5 mgKOH/g, more preferably from 10 to 120 mgKOH/g and even more preferably 20 to 80 mgKOH/g. When the hydroxyl group value of the unmodified polyester (ii) is less than 5 mgKOH/g, it is hard for the toner to have both the high temperature preservability and low temperature fixability. The acid value of the unmodified polyester (ii) is normally from 1 to 30 mgKOH/g, preferably from 5 to 20 mgKOH/g and more preferably from 1 to 15 mgKOH/g. By adding the unmodified polyester (ii) having such an acid value, the resultant toner tends to be negatively charged.

[0039]

The modified polyester (i) of the present invention preferably has a glass transition temperature (Tg) of from 50 to 70 °C, and more preferably from 55 to 65 °C. When the glass transition temperature is lower than 50 °C, the high temperature preservability of the toner deteriorates. When the glass transition temperature is higher than 70 °C, the low temperature fixability becomes insufficient. In addition, the glass transition temperature of the unmodified polyester (ii) is preferably from 35 to 55 °C. When the unmodified polyester (ii) has a glass transition temperature lower than 35 °C, the toner may be blocked when the toner is stored in a high temperature environment. When the toner is stored at a temperature higher than 55 °C, fixability becomes insufficient and the minimum fixable fixing temperature may increase.

Since an unmodified polyester resin coexists with a modified polyester resin, the dry toner of the present invention can have a good high temperature preservability even when the toner has a relatively low glass transition temperature compared with known toners formed of polyesters

[0040]

The toner of the present invention preferably has a storage modulus of elasticity of 10,000 dyne/cm^2 at a temperature (TG′) not lower than 100 °C, and more preferably from 110 to 200 °C when measured at a frequency of 20 Hz. When the temperature TG′ is lower than 100 °C, the toner has poor hot offset resistance. In addition, the toner of the present invention preferably has a viscosity of 1000 poise at a temperature (Tη) not higher than 180 °C, and more preferably from 90 to 160 °C. When the temperature Tη is higher than 180 °C, the low temperature fixability of the toner deteriorates. Namely, in view of compatibility between low temperature fixability and hot offset resistance, the temperature TG′ of the toner is preferably higher than the temperature Tη, i.e., the difference between TG′ and Tη (TG′ −Tη) is preferably not less than 0 °C. More preferably, the difference is not less than 10 °C and even more preferably not less than 20 °C. There is no upper limit to the difference. However, in view of compatibility between high temperature preservability and low temperature fixability, the difference (TG′ - Tη) is preferably from 0 to 100 °C, more preferably from 10 to 90 °C, and even more preferably from 20 to 80 °C.

[0041]

(Release Agent)

The toner of the present invention can include othe components, indicating but not limited to, a wax as well as a toner binder and a colorant. Known waxes for use in conventional toners can be used in the toner of the present invention. The wax can be used singly or in a combination of two or more waxes as desired.

Suitable releasing agents include, but are not limited to polyolefin waxes (e.g., polyethylene waxes and polypropylene waxes); hydrocarbons having a long chain (e.g., paraffin waxes and SASOL waxes); and waxes having a carbonyl group. Among these materials, waxes having a carbonyl group are preferably used for the toner of the present invention.

Specific preferred examples of the waxes including a carbonyl group include polyalkanoic acid esters such as carnauba waxes, montan waxes, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerin tribehenate, and 1,18-octadecanediol distearate; polyalkanol esters such as tristearyl trimellitate, and distearyl maleate; polyalkanoic acid amides such as ethylenediamine dibehenylamide; polyalkylamides such as trimellitic acid tristearylamide; dialkyl ketone such as distearyl ketones; etc. Among these materials, polyalkanoic acid esters are more prefeered. The waxes for use in the present invention normally have a melting point of from 40 to 160 °C, preferably from 50 to 120 °C and more preferably from 60 to 90 °C. Waxes having a melting point lower than 40 °C adversely affect high temperature preservability and waxes having a melting point higher than 160 °C tend to cause cold offset when fixed at a low temperature. In addition, the wax preferably has a melting viscosity of from 5 to 1000 cps, and more preferably from 10 to 100 cps, at a temperature 20 °C higher than the melting point thereof. Waxes having a melting viscosity higher than 1000 cps deteriorates hot offset resistance and low temperature fixability.

The content of a wax contained in the toner is normally from 0 to 40% by weight and preferably from 3 to 30% by weight.

[0042]

(Charge controlling agent)

The toner of the present invention optionally includes a charge controlling agent. Known charge controlling agents can be used for the toner of the present invention either singly or as a combination of 2 or more. Specific preferred examples of the charge controlling agents include nigrosine dyes, triphenyl methane dyes, metal compounds dyes including chrome, chelate compounds of molybdic acid, Rhodamine dyes, alkoxyamines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts), alkylamides, phosphor and compounds including phosphor, tungsten and compounds including tungsten, fluorine-containing activators, metal salts of salicylic acid, metal salts of salicylic acid derivatives, etc.

Specific more preferred examples of the charge controlling agents include BONTRON 03 (nigrosine dyes), BONTRON P-51 (quaternary ammonium salt), BONTRON E-82 (metal complex of oxynaphthoic acid), BONTRON S-34 (azo dyes containing a metal), BONTRON E-84 (metal complex of salicylic acid), and BONTRON E-89 (phenolic condensation product), which are manufactured by Orient Chemical Industries Co., Ltd.; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt), which are manufactured by Hodogaya Chemical Co., Ltd.; COPY CHARGE PSY VP2038 (quaternary ammonium salt), COPY BLUE PR (triphenyl methane derivative), COPY CHARGE NEG VP2036 and COPY CHARGE NX VP434 (quaternary ammonium salt), which are manufactured by Hoechst AG; LRA-901, and LR-147 (boron complex), which are manufactured by Japan Carlit Co., Ltd.; copper phthalocyanine, perylene, quinacridone, azo pigments, and polymers having a functional group such as a sulfonate group, a carboxyl group, a quaternary ammonium group, etc.

[0043]

The content of charge controlling agents in the toner of the present invention depends on the kind of the toner binder resin used, whether other additives are used, and the toner manufacturing method used inclusive of the dispersing method and therefore there is no specific limitation thereto. However, it is preferable that the charge controlling agent be used in an amount of from 0.1 to 10 parts by weight per 100 parts by weight of the binder resin and more preferably of from 0.2 to 5 parts by weight. When the amount is greater than 10 parts by weight, the toner is so excessively charged that electrostatic attraction force between the toner and a developing roller increases, resulting in deterioration of fluidity of the developer and deterioration of image density.

These charge controlling agents and releasing agents can be fused and kneaded with a master batch and a resin or can be added when dissolved and dispersed in an organic solvent.

[0044]

(External additive)

In order to improve fluidity, developability and chargeability of the toner coloring particles (mother toner particles), inorganic particulates can be preferably added thereto. Such inorganic particulates preferably have a primary particle diameter of from 5 nm to 2 μm and more preferably of from 5 to 500 nm. In addition, it is preferable that a specific surface area thereof be from 20 to 500 m^2/g when measured by a BET method. The content of the inorganic particulates in the toner is preferably from 0.01 to 5.0% by weight, and more preferably from 0.01 to 2.0% by weight, based on the total weight of the toner.

Specific preferred examples of such inorganic particulates include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, sand-lime, diatom earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, etc.

[0045]

Other than the above-mentioned, particulate polymers, (which can be prepared by a method such as soap free emulsion polymerization, suspension polymerization or dispersion polymerization), such as copolymers of polystyrene, methacrylic acid esters and acrylic acid esters, particulate polycondensation compounds (e.g., silicone resins, benzoguanamine resins and nylons), and polymers of thermosetting resins can also be used.

[0046]

When such external additives (fluidizers) are surface treated to improve hydrophobicity, good fluidity and chargeability can be maintained even in a high humidity environment. Suitable surfactants for use in the hydrophobizing treatment include silane coupling agents, silylation agents, silane coupling agents having a fluorinated alkyl group, organic titanate coupling agents, aluminum coupling agents, silicone oils, modified silicone oils, etc.

[0047]

The toner can optionally include a cleanability improving agent to easily remove toner particles which remain on an image carrier such as a photoreceptor and a first transfer medium after a toner image is transferred.

Specific preferred examples of such cleanability improving agents include fatty acids and their metal salts such as stearic acid, zinc stearate, and calcium stearate; and particulate polymers such as polymethyl methacrylate and polystyrene, which can be manufactured by a method such as soap-free emulsion polymerization methods. Such particulate polymers preferably have a relatively sharp particle diameter distribution and a volume average particle diameter of from 0.01 to 1 µm.

[0048]

(Manufacturing method)

An example of a method for manufacturing the dry toner of the present invention will be described. The toner binders can be manufactured, for example, by the following method includeing the steps of:

(1) heating polyol (1) and polycarbonic acid (2) to 150 to 280 °C in the presence of a known esterification catalyst such as tetra butoxy titanate and dibutyl tin oxide;
(2) decreasing the pressure on a necessity basis while removing the generated water to obtain a polyester having a hydroxyl group;
(3) reacting the polyester with polyisocyanate (3) at temperatures in the range of from 40 to 140 °C to obtain a prepolymer (A) having an isocyanate group; and
(4) reacting the prepolymer (A) with amine (B) at temperatures in the range of from 0 to 140 °C to obtain modified polyester (i).

A solvent can be optionally used for the reaction of the polyester with polyisocyanate (3) and the reaction of the polymer (A) with the amine (B).

Suitable solvents include, but are not limited to, aromatic solvents such as toluene and xylene; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters such as acetic ether;

amides such as dimethyl formamide and dimethyl acetamide; and ethers such as tetrahydrofuran which are inactive to isocyanate (3). When the polyester (ii) which is not modified with a urea linkage is used, the polyester (ii) can be prepared in the method similar to that for the polyester having a hydroxyl group. The polyester (ii) is dissolved in the resultant solution of (i) mentioned above to be mixed.

[0049]

The dry toner can be manufactured by the following method, but the manufacturing method is not limited thereto.

(Fusing, kneading and pulverizing method)

(1) Toner constituents such as a binder resin including the modified polyester resin (i), a charge controlling agent and a pigment are mechanically mixed. A typical mixer having a revolving blade can be used under conventional conditions. There is no restriction in this mixing process.

(2) After the mixing process, the mixture is set in a kneading machine for fusing and kneading. As fusing and kneading machine, continuous kneading machines such as one-shaft kneading machines and two-shaft kneading machines, and batch type kneading machines such as roll mills can be used.

It is important that fusing and kneading are performed in such a way that the molecular chains of the binder resin are not sheared. Specifically, the temperature for fusing and kneading is preferably determined considering the softening point of the toner binder resin. When the fusing and kneading temperature is too low relative to the softening point, excessive shearing occurs. In contrast when the fusing and kneading temperature is too high, dispersion does not proceed.

[0050]

(3) After the fusing and kneading process mentioned above, pulverize the kneaded toner constituents. In this pulverization process, it is preferable to roughly pulverize the kneaded toner constituents followed by fine pulverizing. In this process, the

kneaded toner constituent is preferably pulverized by hitting the kneaded toner constituents flowing in a jet air stream against a collision board or by passing through a narrow gap between a rotor which mechanically revolves and a stator.

[0051]

(4) After the pulverization process, the pulverized toner constituents are classified in an air stream using a centrifugal force, etc. to prepare toner particles having a predetermined particle diameter, for example, such as an average particle diameter of from 5 to 20 μm.

[0052]

In addition, when preparing a toner, an inorganic particulate such as the hydrophobic silica particulate mentioned above can be optionally added to the thus manufactured toner particles to improve fluidity, preservability, developability and transferability of the toner.

In the process of mixing the external additive, a conventional powder mixer is used. It is preferable that the powder mixer be equipped with a jacket and the like to adjust the internal temperatures thereof. In order to change stresses on the external additive, the external additive may be added in separate times or step by step.

It is also possible to change stress by varying the number of rotation, tumbling speed, and mixing time and temperature. For example, a method in which a strong stress is first applied and then a relatively weak stress is applied, or vice versa can be used.

Specific preferred examples of mixing facilities include v-type mixers, rocking mixers, Loedige Mixers, Nauta mixers and Henschel mixers.

[0053]

There are various methods useful for rounding the obtained toner particles as follows: a mechanical pulverization method including the steps of: (1) fusing/kneading the toner constituents including a toner binder and a colorant, (2) finely pulverizing the kneaded toner constituents and (3) mechanically rounding the finely pulverized toner constituents using a hybridizer and MECHANOFUSION; a spray drying method including the steps of: (1) dissolving and dispersing toner constituents including at least a binder resin and a colorant in a solvent which can dissolve the toner binder; and (2) removing the solvent using a spray drying device; and a method including the steps of: heating toner constituents in an aqueous medium. The rounding methods are not limited thereto.

[0054]

(Toner manufacturing method in aqueous medium)

Suitable aqueous media for use in the method of manufacturing the toner of the present invention include water and mixtures of water and a solvent which can be mixed with water. Specific preferred examples of such a solvent include alcohols (e.g., methanol, isopropanol and ethylene glycol), dimethylformamide, tetrahydrofuran, cellosolves (e.g., methyl cellosolve), lower ketones (e.g., acetone and methyl ethyl ketone), etc.

[0055]

Toner particles can be prepared by reacting a dispersion element including the prepolymer (A) having an isocyanate group with an amine (B) in an aqueous medium or by dispersing the modified polyester (i) which is prepared in advance in an aqueous medium. In order to stably disperse the polyester (i) or the prepolymer (A) in an aqueous medium, a method in which toner constituents including the modified polyester (i) or the prepolymer (A) are added in an aqueous medium and dispersed by a shearing force is preferably used. Although the prepolymer (A) and other toner components (hereinafter referred to as toner materials) such as a colorant, a colorant master batch, a releasing agent, a charge controlling agent and an unmodified polyester resin (ii) can be mixed in an aqueous medium when forming a dispersion element, it is preferable that the toner materials be mixed first and then the mixture added and dispersed in an aqueous medium. In the present invention, the other toner materials such as a colorant, a releasing agent and a charge controlling agent are not necessarily mixed at the time of forming particles in an aqueous medium but can be added after particles are formed. For example, a colorant can be added by a method in which particles including no colorant are formed and then dyed by a known dyeing method.

[0056]

There is no particular restriction for the dispersion method. Low speed shearing methods, high speed shearing methods, friction methods, high pressure jet methods, ultrasonic methods, etc. can preferably be used. Among these methods, high speed shearing methods are more preferable because particles having a particle diameter of from 2 μm to 20 μm can be easily prepared.

When a high speed shearing type dispersion machine is used, there is no particular limit to the rotation speed thereof, but the rotation speed is typically from 1000 to 30000 rpm, and preferably from 5000 to 20000 rpm. The dispersion time is also not particularly limited, but is typically from 0.1 to 5 minutes for a batch production method. The temperature in the dispersion process is typically from 0 to 150 °C (under pressure), and preferably from 40 to 98 °C. The dispersion process is preferably performed at a high temperature because a dispersion element including the modified polyester (i) or the prepolymer (A) has a low viscosity at a high temperature.

[0057]

The amount of the aqueous medium used is normally from 50 to 2000 parts by weight and preferably from 100 to 1000 parts by weight per 100 parts by weight of toner material including the modified polyester (i) or the prepolymer (A). When the amount of the aqueous medium is too small, the toner materials do not disperse well and thereby toner particles having a predetermined particle diameter cannot be obtained. When the amount is too large, the manufacturing cost increases. Dispersants can be used if necessary. It is preferable to use a dispersant because the toner can have a sharp particle diameter distribution and can be stably dispersed.

[0058]

Specific preferred examples of the dispersants which are used for emulsifying and dispersing an oil phase liquid, in which toner constituents are dispersed, in an aqueous phase liquid, include anionic surfactants such as alkylbenzene sulfonic acid salts, α-olefin sulfonic acid salts, and phosphoric acid esters; cationic surfactants such as amine salts (e.g., alkyl amine salts, aminoalcohol fatty acid derivatives, polyamine fatty acid derivatives and imidazoline), and quaternary ammonium salts (e.g., alkyltrimethyl ammonium salts, dialkyldimethyl ammonium salts, alkyldimethyl benzyl ammonium salts, pyridinium salts, alkyl isoquinolinium salts and benzethonium chloride); nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and ampholytic surfactants such as alanine, dodecyldi(aminoethyl)glycin, di(octylaminoethyle)glycin, and N-alkyl-N,N-dimethylammonium betaine.

[0059]

A surfactant having a fluoroalkyl group is particularly effective even in an extremely small amount. Specific preferred examples of anionic surfactants having a fluoroalkyl group include fluoroalkyl carboxylic acids having 2 to 10 carbon atoms and their metal salts, disodium perfluoro octanesulfonyl glutamate, sodium 3-{ omega-fluoroalkyl(C6-C11)oxy} -1-alkyl(C3-C4) sulfonate, sodium 3-{ omega-fluoroalkanoyl(C6-C8)-N-ethylamino} -1-propanesulfonate, fluoroalkyl(C11-C20) carboxylic acids and their metal salts, perfluoroalkylcarboxylic (C7-C13) acids and their metal salts, perfluoroalkyl(C4-C12)sulfonate and their metal salts, perfluorooctanesulfonic acid diethanol amides, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfone amide, perfluoroalkyl(C6-C10)sulfoneamidepropyltrimethylammonium salts, salts of perfluoroalkyl(C6-C10)-N-ethylsulfonyl glycine, monoperfluoroalkyl(C6-C16)ethylphosphate esters, etc.

[0060]

Specific preferred examples of the marketed products of such surfactants include SURFLON S-111, S-112 and S-113, which are manufactured by Asahi Glass Co., Ltd.; FRORARD FC-93, FC-95, FC-98 and FC-129, which are manufactured by Sumitomo 3M Ltd.; UNIDYNE DS-101 and DS-102, which are manufactured by Daikin Industries, Ltd.; MEGAFACE F-110, F-120, F-113, F-191, F-812 and F-833, which are manufactured by Dainippon Ink and Chemicals, Inc.; ECTOP EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201 and 204, which are manufactured by Tohchem Products Co., Ltd.; and FUTARGENT F-100 and F150, which are manufactured by Neos.

[0061]

Specific preferred examples of the cationic surfactants include primary, secondary and tertiary aliphatic amines having a fluoroalkyl group, aliphatic quaternary ammonium salts such as perfluoroalkyl(C6-C10)sulfoneamidepropyltrimethylammonium salts, benzalkonium salts, benzetonium chloride, pyridinium salts, imidazolinium salts. Specific preferred examples of the marketed products thereof include SURFLON S-121 (from Asahi Glass Co., Ltd.); FRORARD FC-135 (from Sumitomo 3M Ltd.); UNIDYNE DS-202 (from Daikin Industries, Ltd.); MEGAFACE F-150 and F-824 (from Dainippon Ink and Chemicals, Inc.); ECTOP EF-132 (from Tohchem Products Co., Ltd.); FUTARGENT F-300 (from Neos); etc.

[0062]

In addition, inorganic dispersants, which are hardly soluble in water, such as tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, and hydroxyapatite can also be used.

[0063]

Further, it is possible to stabilize dispersion droplets using a polymeric protection colloid. Specific preferred examples of such protection colloids include homopolymers and copolymers prepared using monomers such as acids (e.g., acrylic acid, methacrylic acid, α-cyanoacrylic acid, α-cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid and maleic anhydride), acrylic monomers having a hydroxyl group (e.g., β-hydroxyethyl acrylate, β-hydroxyethyl methacrylate, β-hydroxypropyl acrylate, β-hydroxypropyl methacrylate, γ-hydroxypropyl acrylate, γ-hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethyleneglycolmonoacrylic acid esters, diethyleneglycol monomethacrylic acid esters, glycerinmonoacrylic acid esters, N-methylolacrylamide and N-methylolmethacrylamide), vinyl alcohol and its ethers (e.g., vinyl methyl ether, vinyl ethyl ether and vinyl propyl ether), esters of vinyl alcohol with a compound having a carboxyl group (i.e., vinyl acetate, vinyl propionate and vinyl butyrate); acrylic amides (e.g, acrylamide, methacrylamide and diacetoneacrylamide) and their methylol compounds, acid chlorides (e.g., acrylic acid chloride and methacrylic acid chloride), and monomers and copolymers having a nitrogen atom or an heterocyclic ring having a nitrogen atom (e.g., vinyl pyridine, vinyl pyrrolidone, vinyl imidazole and ethylene imine).

In addition, polymers such as polyoxyethylene compounds (e.g., polyoxyethylene, polyoxypropylene, polyoxyethylenealkyl amines, polyoxypropylenealkyl amines, polyoxyethylenealkyl amides, polyoxypropylenealkyl amides, polyoxyethylene nonylphenyl ethers, polyoxyethylene laurylphenyl ethers, polyoxyethylene stearylphenyl esters, and polyoxyethylene nonylphenyl esters); and cellulose compounds such as methyl cellulose, hydroxyethyl cellulose and hydroxypropyl cellulose, can also be used as the polymeric protective colloid.

[0064]

In order to remove an organic solvent from the thus prepared emulsified dispersion, a method in which the emulsion is gradually heated to substantially completely evaporate the organic solvent included in the drops of the oil phase liquid can be used. Alternatively, a method in which the emulsion is sprayed in a dry environment to remove the nonaqueous solvent in the droplets, resulting in formation of toner particles, and thereafter water in the dispersion is evaporated, can be used. Specific preferred examples of such a dry environment include gases of air, nitrogen, carbon dioxide, combustion gas, etc. It is preferable that those gases be heated to a temperature not lower than the boiling point of the solvent having the highest boiling point among the solvents used in the emulsion. Toner particles having desired properties can be rapidly prepared by performing this treatment using a spray dryer, a belt dryer, a rotary kiln, or the like.

[0065]

When compounds such as calcium phosphate which are soluble in an acid or alkali are used as a dispersion stabilizer, the resultant toner particles are preferably mixed with an acid such as hydrochloric acid to dissolve calcium phosphate, followed by washing with water to remove calcium phosphate from the toner particles. In addition, calcium phosphate can be removed using a zymolytic method.

[0066]

When a dispersant is used, the resultant particles are preferably washed after the particles are subjected to an elongation and/or a crosslinking reaction to impart good chargeability to the particles.

[0067]

Further, in order to reduce the viscosity of the dispersion of the toner materials, a solvent which dissolves the modified polyester (i) or the prepolymer (A) can be added. It is preferable to use such a solvent to allow the resultant toner to have a sharp particle diameter distribution. Volatile solvents having a boiling point lower than 100 °C are preferably used as the solvent because such solvents can be removed with ease after the particles are formed.

Specific preferred examples of such a solvent include toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methyl ethyl ketone, and methyl isobutyl ketone. These solvents can be used alone or in combination. Among these solvents, aromatic solvents such as toluene and xylene; and halogenated hydrocarbons such as methylene chloride, 1,2-dichloroethane, chloroform, and carbon tetrachloride are more preferably used.

The addition amount of such a solvent is not limited, but is generally from 0 to 300 parts by weight, preferably from 0 to 100 parts by weight and more preferably from 25 to 70 parts by weight, per 100 parts by weight of the prepolymer (A) used. When such a solvent is used to prepare a particle dispersion, the solvent is removed upon application of heat thereto under a normal or reduced pressure after the particles are subjected to an extension treatment and/or a crosslinking treatment.

[0068]

The reaction time of extension and/or crosslinking is determined depending on the reacting property of the isocyanate structure of the prepolymer (A) with the amine (B) used, but the reaction time is generally from 10 minutes to 40 hours, and preferably 2 hours to 24 hours. The reaction temperature is generally from 0 to 150 °C and preferably from 40 to 98 °C. In addition, known catalysts can optionally be used. Specific preferred examples of the catalysts include dibutyltin laurate and dioctyltin laurate.

[0069]

In order to remove an organic solvent from the thus prepared emulsified dispersion, a method in which the emulsion is gradually heated to substantially completely evaporate the organic solvent included in the drops of the oil phase liquid can be used. Alternatively, a method in which the emulsion is sprayed in a dry environment to remove the nonaqueous solvent in the droplets, resulting in formation of toner particles, and thereafter water in the dispersion is evaporated, can be used. Specific preferred examples of such a dry environment include gases of air, nitrogen, carbon dioxide, combustion gas, etc. It is preferable that those gases be heated to a temperature not lower than the boiling point of the solvent having the highest boiling point among the solvents used in the emulsion. Toner particles having desired properties can be rapidly prepared by performing this treatment using a spray dryer, a belt dryer, a rotary kiln, or the like.

[0070]

When the resultant toner has a wide particle diameter distribution at the time of emulsification dispersion and the wide particle diameter distribution is maintained during a washing and drying treatment, it is possible to prepare a toner having a desired particle diameter distribution by classifying the produced toner.

Fine particles can be removed from the toner by classification using a cyclone, a decanter or a device using a centrifugal force while the toner is in a liquid. It is also possible to classify a toner which is obtained by drying the dispersion. However classification in a liquid is preferable in the light of efficiency. The thus obtained unwanted fine particles and coarse particles can be returned to the kneading process to form particles again even when those fine particles and coarse particles are wet.

It is preferable to remove the used dispersant from the obtained dispersion liquid as much as possible at the same time of the classification mentioned above.

[0071]

The thus obtained toner powder can be mixed with fine particles of other materials such as a releasing agent, a charge controlling agent, a fluidizer agent and a colorant. These materials can be fixed and fused on the surface of the toner powder by, for example, a mechanical impact on the powder mixture in order to prevent the particles from detaching from the toner particles.

Specific preferred examples of the method include: a method of making an impact on a mixture with a blade rotating at a high speed and another method of colliding particles against each other or complex particles against a collision board.

Specific more preferred examples of such mechanical impact applicators include ONG MILL (manufactured by Hosokawa Micron Co., Ltd.), modified I TYPE MILL in which the air pressure for pulverizing is reduced (manufactured by Nippon Pneumatic Mfg. Co., Ltd.), HYBRIDIZATION SYSTEM (manufactured by Nara Machine Co., Ltd.), KRYPTRON SYSTEM (manufactured by Kawasaki Heavy Industries, Ltd.), and automatic mortars.

[0072]

(Carrier for a two component developer)

The toner of the present invention can be used for a two component developer in which the toner is mixed with a magnetic carrier. The weight ratio (T/C) of the toner (T) to the carrier (C) is preferably from 1/100 to 10/100.

Suitable carriers for use in such two component developers include any known carrier materials such as iron powders, ferrite powders, magnetite powders, magnetic resin carriers, which have a particle diameter of from about 20 μm to about 200 μm. The surface of the carriers may be coated with a resin.

Specific preferred examples of such resins to be coated on the carriers include amino resins such as urea-formaldehyde resins, melamine resins, benzoguanamine resins, urea resins, and polyamide resins, and epoxy resins. In addition, polyvinyl or polyvinylidene resins such as acrylic resins, polymethylmethacrylate resins, polyacrylonitirile resins, polyvinyl acetate resins, polyvinyl alcohol resins, polyvinyl butyral resins, polystyrene resins, styrene-acrylic copolymers, halogenated olefin resins such as polyvinyl chloride resins, polyester resins such as polyethyleneterephthalate resins and polybutyleneterephthalate resins, polycarbonate resins, polyethylene resins, polyvinyl fluoride resins, polyvinylidene fluoride resins, polytrifluoroethylene resins, polyhexafluoropropylene resins, vinylidenefluoride-acrylate copolymers, vinylidenefluoride-vinylfluoride copolymers, fluoroterpolymers such as terpolymer of tetrafluoroethylene, vinylidenefluoride and other monomers including no fluorine atom, and silicone resins can be used.

If desired, an electroconductive powder may be included in the coating resin. Specific preferred examples of such electroconductive powders include metal powders, carbon blacks, titanium oxides, tin oxides, and zinc oxides. The average particle diameter of such electroconductive powders is preferably not greater than 1 μm. When the particle diameter is greater than 1 μm, it is hard to control the electrical resistance thereof.

[0073]

The toner of the present invention can also be used as a single component magnetic developer or a single component non-magnetic developer, which does not use a carrier.

[0074]

[Examples]

The present invention will be described with reference to examples but not limited thereto. In the descriptions in the following examples, the numbers represent weight ratios in parts.

[0075]

Example 1

(Synthesis of toner binder)

The following components were contained in a reaction container having a condenser, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230 °C under normal pressure.

Adduct of bisphenol A with 2 moles of ethylene oxide	724
Isophthalic acid	276
Dibutyl tin oxide	2

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg. Subsequent to cooling down to 160 °C, 32 parts of phthalic anhydride were added thereto to perform a reaction for 2 hours. Subsequent to cooling down to 80 °C, 188 parts of isophorone diisocyanate were added thereto in ethyl acetate to react for 2 hours. Thus, a prepolymer (1) containing an isocyanate group was prepared. Then 267 parts of the prepolymer (1) and 14 parts of isophorone diamine were reacted for 2 hours at 50 °C. Thus, a urea-modified polyester (1) was prepared. The urea-modified polyester (1) had a weight average molecular weight of 64000.

Similarly, 724 parts of adduct of bisphenol A with 2 mole ethylene oxide and 276 parts of terephthalic acid were reacted for 8 hours at 230 °C under normal pressure to perform polycondensation. Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg. Thus an unmodified polyester (a) was obtained. The unmodified polyester (a) had a peak molecular weight of 5000. Two hundred (200) parts of the urea-modified polyester (1) and 800 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1). Thus, an ethyl acetate/methyl ethyl ketone solution of the toner binder (1) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (1). The toner binder (1) had a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

The following components were placed in a beaker and stirred at 60 °C by a TK type HOMOMIXER at 12000 rpm to be uniformly dissolved and dispersed.

Ethyl acetate/methyl ethyl ketone solution of the toner binder (1) mentioned above	240
Pentaerythritol tetrabehenate (melting point of 81 °C, fusing viscosity of 25 cps)	20
Carbon black (PH of 4.5)	10

Further, 706 parts of ion exchanged water, 294 parts of 10% hydroxyapatite suspension (SUPERTITE 10 from Nippon Chemical Industrial Co., Ltd) and 0.2 parts of dodecyl benzene sulphonic sodium were contained in a beaker to prepare a dispersion. The dispersion was heated to 60 °C, and then stirred with a TK HOMOMIXER at 12000 rpm. Then adding the toner material liquid prepared above was added thereto. After stirring for 10 minutes, the mixture was moved to a flask having a stirrer and a thermometer and heated to 98 °C to remove the solvent therein. After filtering, washing and drying, the resultant powder was subjected to air separating. Thus mother toner particles were obtained with a volume average particle diameter (Dv) of 6.1 µm, a number average particle diameter (Dp) of 5.2 µm, Dv/Dp of 1.17 and volume resistivity of 10.6 (LogΩcm).

Further, 100 parts of the mother toner particles, 0.5 parts of a hydrophobic silica and 0.5 parts of a hydrophobic titanium oxide were mixed with a Henschel mixer and thus the toner (1) of the present invention was obtained. The results are shown in Table 1.

[0076]

Example 2

(Synthesis of toner binder)

The following components were subjected to polycondensation in the same way as in Example 1.

Adduct of bisphenol A with 2 moles of ethylene oxide	334
Adduct of bisphenol A with 2 moles of propylene oxide	334
Isophthalic acid	274
Trimellitic acid anhydride	20

Then 154 parts of isophoron diisocyanate were added and reacted to obtain a prepolymer (2). Further, 213 parts of the prepolymer (2), 9.5 parts of isophoron diamine and 0.5 parts of dibutyl amine were reacted in the same way as in Example 1 and thus a urea-modified polyester (2) having a weight average molecular weight of 79000 was obtained. Two hundred parts of the urea-modified polyester (2) and 800 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate solution of the toner binder (2) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (2). The toner binder (2) has a peak molecular weight of 5000, a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

The toner (2) of the present invention was obtained in the same manner as illustrated in Example 1 except that the temperature of dissolution and dispersion was changed to 50 °C. The mother particle of the toner had a volume average particle diameter (Dv) of 5.4 μm, a number average particle diameter (Dp) of 4.6 μm and Dv/Dp of 1.17. The results are shown in Table 1.

[0077]

Comparative Example 1

(Synthesis of toner binder)

The same toner binder as in Example 1 was used.

(Manufacturing of toner)

A toner was prepared in the same manner as illustrated in Example 1 except that carbon black having a PH of 8.5 was used instead of the carbon black used in Example 1. The obtained comparative toner (1) had a volume average particle diameter of 6 μm. The mother toner particles had a volume average particle diameter (Dv) of 6.2 μm, a number average particle diameter (Dp) of 5.1 μm and Dv/Dp of 1.22. The results are shown in Table 1.

[0078]

(Table 1)

Toner No.	Fluidity	Minimum fixing temperature	Hot offset	Volume resistivity	Amount of charge (-μc/g)	
					At start	After 30000 prints
Example 1	0.41	135 °C	220 °C	10.7	22	20
Example 2	0.40	145 °C	Not lower than 230 °C	10.8	21	19
Compar-ative Exampl	0.39	130 °C	220 °C	9.6	16	8

e 1						

[0079]

Example 3

(Manufacturing of toner)

Thirty parts of the urea-modified polyester (1) and 970 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl ethyl ketone solution of a toner binder (3) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (3). The toner binder (3) had a peak molecular weight of 5000, a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

A toner (3) according to the present invention was obtained in the same manner as illustrated in Example 2 except that the toner binder (2) was replaced with the toner binder (3) and the addition amount of carbon black was changed to 8 parts. The mother toner particles had a volume average particle diameter (Dv) of 5.7 μm, a number average particle diameter (Dp) of 4.8 μm and Dv/Dp of 1.19. The results are shown in Table 2.

[0080]

Example 4

(Synthesis of toner binder)

Five hundred parts of the urea-modified polyester (1) and 500 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl ethyl ketone solution of a toner binder (4) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (4). The toner binder (4) had a peak molecular weight of 5000, a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

A toner (4) according to the present invention was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) in Example 1 was replaced by the toner binder (4) and the addition amount of carbon black was changed to 8 parts. The mother toner particles had a volume average particle diameter (Dv) of 6.5 μm, a number average particle diameter (Dp) of 5.5 μm and Dv/Dp of 1.18. The results are shown in Table 2.

[0081]

Comparative Example 2

(Synthesis of toner binder)

The following components were contained in a reaction container having a condenser, a stirrer and a nitrogen introducing tube and reacted for 8 hours at 230 °C under normal pressure.

Adduct of bisphenol A with 2 moles of ethylene oxide	343
Isophthalic acid	166
Dibutyl tin oxide	2

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg. Subsequent to cooling down to 80 °C, 14 parts of toluene diisocyanate were added thereto in the presence of toluene and reacted for 5 hours at 110 °C. After the solvent thereof was removed, a urethane modified polyester having a molecular weight of 98000 was obtained. Similar to Example 1, 363 parts of adduct of 2 mole ethylene oxide with bisphenol A and 166 parts of isophthalic acid were subjected to polycondensation. Thus, an unmodified polyester having a peak molecular weight of 3800 and an acid value of 7 mgKOH/g was obtained. Three hundred and fifty (350) parts of the urethane-modified polyester and 650 parts of the unmodified polyester mentioned above were dissolved and mixed in toluene. After removing the solvent thereof, a comparative toner binder (2) was obtained. The comparative toner binder (2) had a Tg of 58 °C.

(Manufacturing of toner)

A toner was obtained using 100 parts of the comparative toner binder (2) and 8 parts of carbon black having a pH of 0.6 according to the following method. Preparatory mixing was performed using a Henschel mixer followed by kneading with a continuous kneading machine. Then the mixture was finely pulverized using a jet mill and classified by an air separator to obtain mother toner particles. Further 100 parts of the mother toner particle, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide were mixed with a Henschel mixer and thus a comparative toner (2) was obtained. The mother toner particles had a volume average particle diameter (Dv) of 7.0 μm, a number average particle diameter (Dp) of 5.2 μm and Dv/Dp of 1.35. The results are shown in Table 2.

[0082]

(Table 2)

Toner No.	Fluidity	Minimum fixing temperature	Hot offset	Volume resistivity	Amount of charge (-μc/g)	
					At start	After 30000 prints
Example 3	0.41	120 °C	230 °C	11.2	20	18
Example 4	0.42	120 °C	230 °C	11.1	21	19
Compar-ative Example 2	0.30	130 °C	220 °C	19	19	10

[0083]

Example 5

(Manufacturing of toner binder)

Seven hundred and fifty (750) parts of the urea-modified polyester (1) and 250 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl

ethyl ketone solution of a toner binder (5) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (5). The toner binder (5) had a peak molecular weight of 5000, a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

A toner was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) was replaced with the toner binder (5). The mother toner particles had a volume average particle diameter (Dv) of 4.4 µm, a number average particle diameter (Dp) of 3.6 µm and Dv/Dp of 1.22. The results are shown in Table 3.

[0084]

Example 6

(Manufacturing of toner binder)

Eight hundred and fifty (850) parts of the urea-modified polyester (1) and 150 parts of the unmodified polyester (a) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl ethyl ketone solution of a toner binder (6) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (6). The toner binder (6) had a peak molecular weight of 5000, a Tg of 62 °C and an acid value of 10 mgKOH/g.

(Manufacturing of toner)

A toner was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) was replaced with the toner binder (6). The mother toner particles had a volume average particle diameter (Dv) of 5.8 µm, a number average particle diameter (Dp) of 4.8 µm and Dv/Dp of 1.21. The results are shown in Table 3.

[0085]

Comparative Example 3

(Synthesis of toner binder)

Three hundred and fifty four (354) parts of adduct of bisphenol A with 2 moles of ethylene oxide and 166 parts of terephthalic acid were reacted to perform polycondensation using 2 parts of dibutyl tin oxide as a catalyst. Thus, a comparative toner binder (3) having a peak molecular weight of 12000, a Tg of 62 °C and an acid value of 10 mgKOH/g was obtained.

(Manufacturing example of toner)

The following components were contained in a beaker and stirred at 50 °C by a TK HOMOMIXER at 12000 rpm to be uniformly dissolved and dispersed.

Comparative toner binder (3) mentioned above	100
Ethyl acetate	200
Carbon black (pH of 7.5)	10

Thus a comparative toner material liquid was obtained. Then the procedure for preparation of the toner in Example 5 was repeated except that the toner material liquid was replaced with the comparative toner material liquid prepared above. The mother toner particles had a volume average particle diameter (Dv) of 6.5 µm, a number average particle diameter (Dp) of 5.1 µm and Dv/Dp of 1.27. The results are shown in Table 3.

[0086]

(Table 3)

Toner No.	Fluidity	Minimum fixing temperature	Hot offset	Volume resistivity	Amount of charge (-µc/g)	
					At start	After 30000 prints
Example 5	0.41	150 °C	230 °C	10.9	20	19
Example 6	0.42	145 °C	230 °C	10.8	22	18
Compar-ative Example 3	0.31	130 °C	160 °C	10.7	20	10

[0087]

Example 7

(Synthesis of toner binder)

The following components were reacted to perform polycondensation for 2 hours at 230 °C under normal pressure.

Adduct of 2 moles of ethylene oxide with bisphenol A	724
Terephthalic acid	276

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg and thus an unmodified polyester (b) having a peak molecular weight of 800 was obtained. Two hundred (200) parts of the urea-modified polyester (1) and 800 parts of the unmodified polyester (b) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl ethyl ketone (1/1) solution of a toner binder (7) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (7). The toner binder (7) had a Tg of 45 °C.

(Manufacturing of toner)

A toner (7) was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) was replaced with the toner binder (7). The mother toner particles had a volume average particle diameter (Dv) of 6.4 μm, a number average particle diameter (Dp) of 5.4 μm and Dv/Dp of 1.19. The results are shown in Table 4.

[0088]

Example 8

(Synthesis of toner binder)

The following components were reacted to perform polycondensation for 4 hours at 230 °C under normal pressure.

Adduct of 2 moles of ethylene oxide with bisphenol A	724
Terephthalic acid	276

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg and thus an unmodified polyester (c) having a peak molecular weight of 2000 was obtained. Two hundred

(200) parts of the urea-modified polyester (1) and 800 parts of the unmodified polyester (c) were dissolved and mixed in 2000 parts of a mixture solvent of ethyl acetate/methyl ethyl ketone (1/1) and thus an ethyl acetate/methyl ethyl ketone (1/1) solution of a toner binder (8) was obtained. A portion of the solution was dried under a reduced pressure to isolate the toner binder (8). The toner binder (8) had a Tg of 52 °C.

(Manufacturing of toner)

A toner (8) was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) was replaced with the toner binder (8). Mother particles of the obtained toner had a volume average particle diameter (Dv) of 5.6 µm, a number average particle diameter (Dp) of 4.9 µm and Dv/Dp of 1.14. The estimated results are shown in Table 4.

Example 9

(Synthesis of toner binder)

The following components were reacted to perform polycondensation for 10 hours at 230 °C under normal pressure.

Adduct of 2 moles of ethylene oxide with bisphenol A	724
Terephthlic acid	276

Then the reaction was further continued for 5 hours under a reduced pressure of from 10 to 15 mmHg and thus an unmodified polyester (d) having a peak molecular weight of 30000 was obtained. Two hundred parts of the urea-modified polyester (1) and 800 parts of the unmodified polyester (d) were dissolved and mixed in 2000 parts of the mixture solvent of ethyl acetate/MEK (1/1) and thus an ethyl acetate/MEK (1/1) solution of a toner binder (9) was obtained. A portion of the solution was dried under a reduced pressure and the toner binder (9) was isolated. The toner binder (9) had a Tg of 69 °C.

(Manufacturing of toner)

A toner (9) was obtained in the same manner as illustrated in Example 1 except that the toner binder (1) was replaced with the toner binder (9). Mother particles of the obtained toner had a volume average particle diameter (Dv) of 6.7 μm, a number average particle diameter (Dp) of 6.2 μm and Dv/Dp of 1.08. The estimated results were shown in Table 4.

[0090]

(Table 4)

Toner No.	Fluidity	Minimum fixing temperature	Hot offset	Volume resistivity	Amount of charge (-μc/g)	
					At start	After 30000 prints
Example 7	0.40	140 °C	220 °C	10.8	23	21
Example 8	0.40	150 °C	230 °C	10.7	21	19
Example 9	0.36	150 °C	230 °C	10.9	25	26

[0091]

[Evaluation method for characteristics]

<Toner particle diameter>

The particle diameter (i.e., volume average particle diameter and number average particle diameter) of a toner was measured with a particle diameter measuring instrument, COULTER COUNTER TAII, manufactured by Coulter Electronics, Inc.

<Powder fluidity>

Bulk density of a toner was measured with a powder tester, manufactured by Hosokawa Micron Ltd. The larger bulk density a toner has, the better fluidity the toner has.

<Amount of charge>

Five (5) parts of a toner and 95 parts of the carrier described below were mixed with a blender for 10 minutes to obtain a developer.

(Carrier)

Core material: Spherical ferrite particle having an average particle diameter of 50 μm.

Coating liquid: A toluene solution of a silicone resin in which an amino silane coupling agent was dispersed.

The coating liquid was spray-coated on the core material in a heated state. The coated carrier was baked and then cooled down. Thus a film resin having an average thickness of 0.2 μm was formed on the core material, to give a coated carrier.

The amount of charge of a developer was measured by a blow-off method using an electrometer. In addition, the developer was installed in PRETER 650 from Ricoh Co., Ltd., and the amount of charge thereof was measured after 30000 prints.

In order to produce good images without background fouling caused by reversely charged toner particles, the amount of charge of the developer preferably falls within the range of from about 15 to about 25 (μc/g) in absolute figure.

<Temperature causing hot offset (HOT)>

Each toner was placed in a commercial color copier (PRETER 550 from Ricoh Co., Ltd.) to produce images. The produced images were visually observed to determine whether hot offset occurs.
Hot offset temperature was defined as the lowest temperature of the fixing roll above which hot offset occurred.

<Minimumfixing temperature>

A copying test was performed using a paper TYPE 6200 manufactured by Ricoh Co., Ltd. and a copier MF-200 from Ricoh Co., Ltd. which is modified such that a TEFLON roller is used as a fixing roller while changing the fixing temperature. Produced images were rubbed to determine the image density remaining ratio defined by the following equation: Image density remaining ratio = ID_a/ID_b, wherein ID_a and ID_b represent the image densities of an image after and before the rubbing, respectively. The minimum fixing temperature was defined as a temperature of the fixing roller above which the image density remaining ratio was not less than 70%.

<Volume resistivity>

(1) A toner pellet was prepared by a method in which 3 grams of a

toner are contained in a cylinder having a diameter of 4 cm and pressed at $6t/cm^2$ for 1 minute using an electric pressing machine, manufactured by Maekawa Testing Co., Ltd.

(2) Volume resistivity of the pellet was measured using a dielectric loss measuring device, i.e., TR-10C type, manufactured by Ando Electric Co., Ltd.

[Measuring condition]

Frequency: 1 KHz

Ratio: $1 \times 1/10^9$

[Mathematical formula 1]

Volume resistivity [$\log(\Omega cm) = \log\{(A \times 100)/\text{Ratio} \times (R-R_0) \times t\}$, wherein t represents a thickness of the sample in mm, A represents an effective electrode area in cm^2, R_0 represent a conductance at zero adjustment in S, and R represents a conductance at measurement in S.

[0092]

[Effects of the Invention]

According to the present invention, a dry toner can be provided which has a small diameter and high electric resistance and is excellent in fluidity, transferability, high temperature preservability, low temperature fixability and hot offset resistance.

In addition, a two-component or single-component developer including the dry toner, a toner container containing the dry toner, an image forming method using the developer, and an image forming apparatus in which the developer is installed, can be provided.

[Brief Description of the Drawings]

[Fig. 1]

Fig.1 is a diagram illustrating a toner shape.

[Reference Numerals]

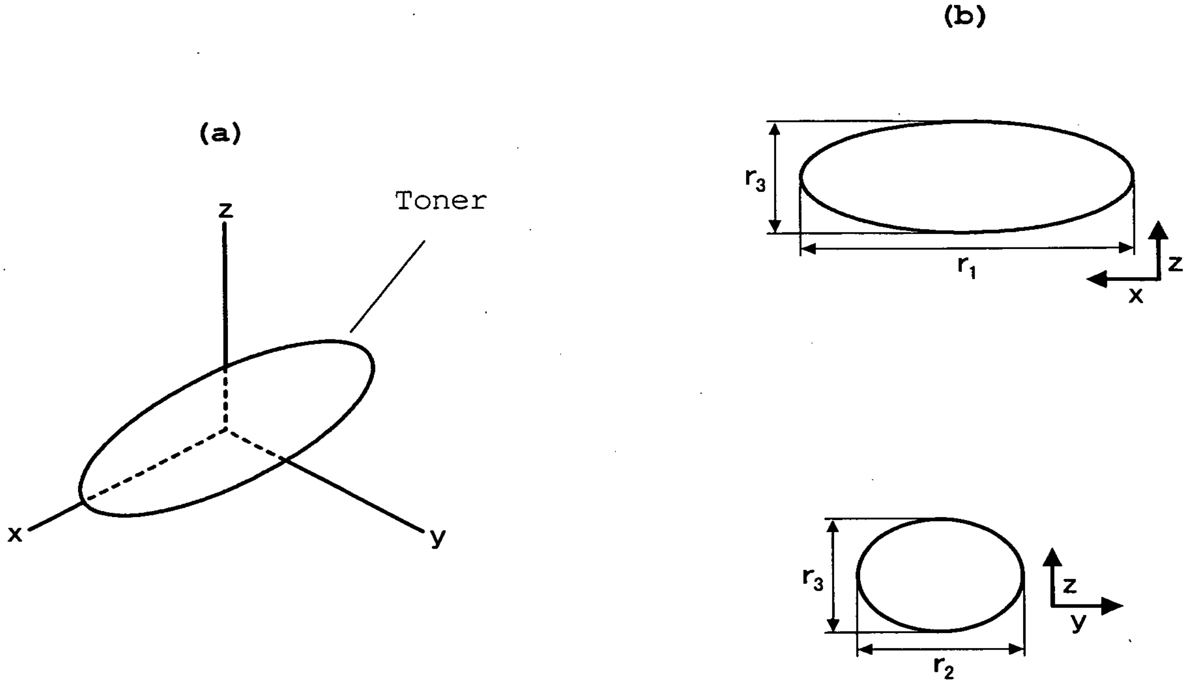
r1: Major axis of the toner

r2: Minor axis of the toner

r3: Thisckness of the toner

[Name of Document] Drawings

[Fig.1]



[Name of Document] Abstract of the Disclosure

[Abstract]

[Objectives of the Invention]

To provide a dry toner which can have a small diameter and high electric resistance and is excellent in fluidity, transferability, high temperature preservability, low temperature fixability and hot offset resistance. In addition, to provide a developer including the dry toner, a toner container containing the dry toner and an image forming method and an image forming apparatus using the developer.

[Means for achieving the Objectives]

A dry toner which is obtained by dissolving or dispersing a toner material composition in an organic solvent and dispersing the resultant toner material composition in an aqueous liquid, including at least a modified polyester serving as a toner binder and a carbon black, wherein the carbon black has a PH not greater than 7. The dry toner has a volume average particle diameter (Dv) of from 3 to 7 μm and a ratio (Dv/Dp) of Dv to a number average particle diameter (Dp) is from 1.00 to 1.25.

[Selected Figure] None